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(54) **PROCESS-BASED APPROACH FOR THE DETECTION OF DEEP GAS INVADING THE SURFACE**

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G01N 33/24 (2006.01)

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CPC ***G01N 33/24*** (2013.01)

(58) **Field of Classification Search**
CPC G01N 33/241; G01N 33/24; G01N 33/00
USPC 436/29, 25
See application file for complete search history.

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(57) **ABSTRACT**

The present invention includes a method for determining the level of deep gas in a near surface formation that includes: measuring CO_2, O_2, CH_4, and N_2 levels in percent by volume from one or more surface or near surface geological samples; adding the water vapor content to the measured CO_2, O_2, CH_4, and N_2 levels in percent by volume; normalizing the gas mixture to 100% by volume or 1 atmospheric total pressure; and determining the ratios of: O_2 versus CO_2 to distinguish in-situ vadose zone CO_2 from exogenous deep leakage CO_2; CO_2 versus N_2 to distinguish whether CO_2 is being removed from the near surface formation or CO_2 is added from an exogenous deep leakage input; or CO_2 versus N_2/O_2 to determine the degree of oxygen influx, consumption, or both; wherein the ratios are indicative of natural in situ CO_2 or CO_2 from the exogenous deep leakage input.

20 Claims, 6 Drawing Sheets

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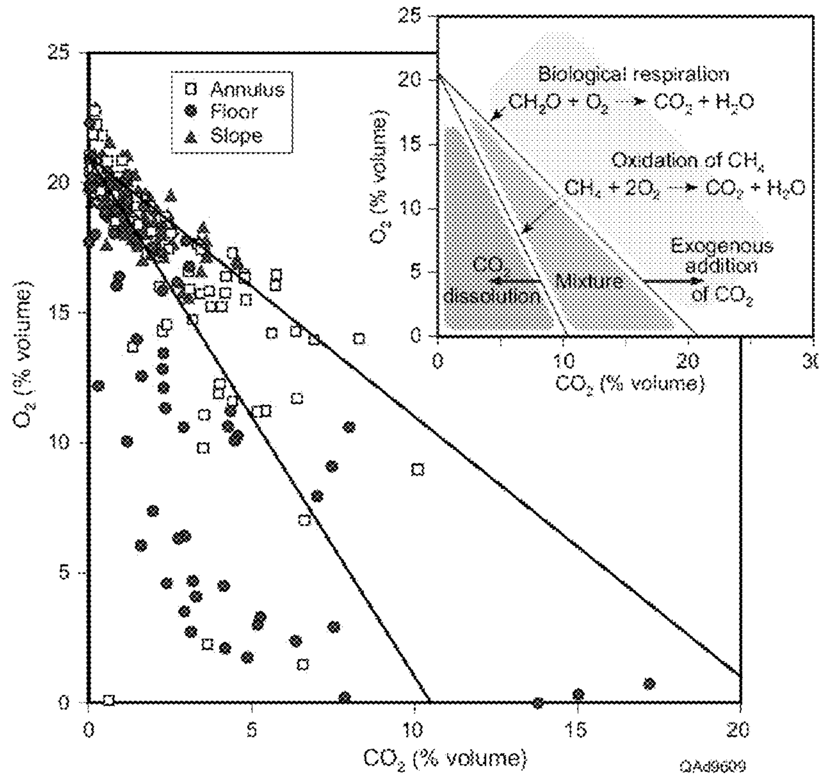


FIGURE 1

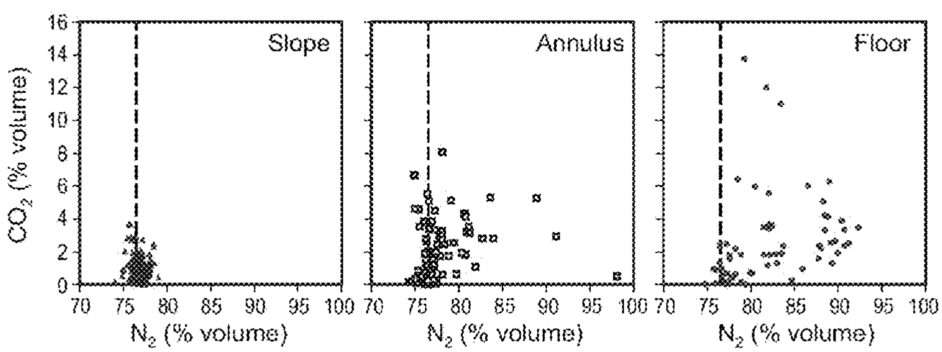


FIGURE 2

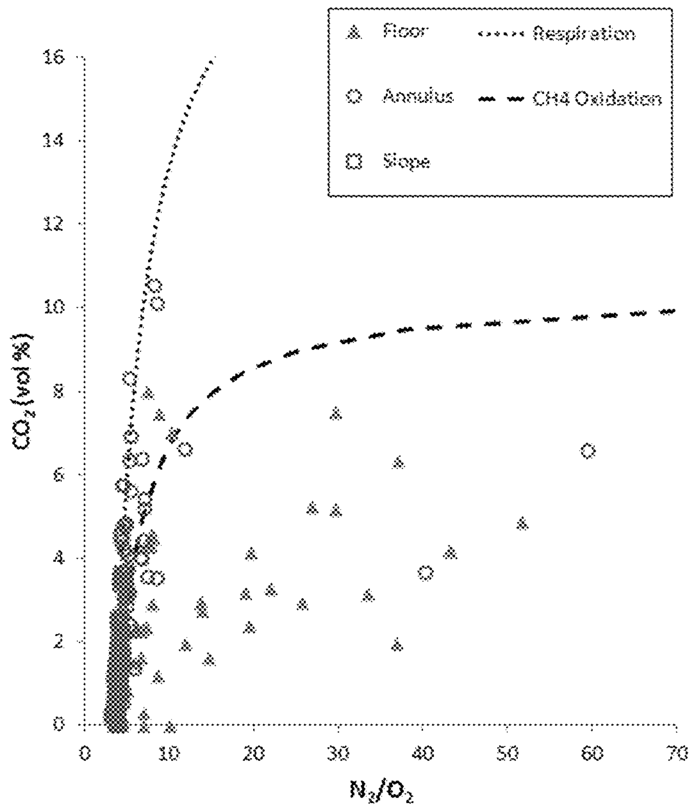
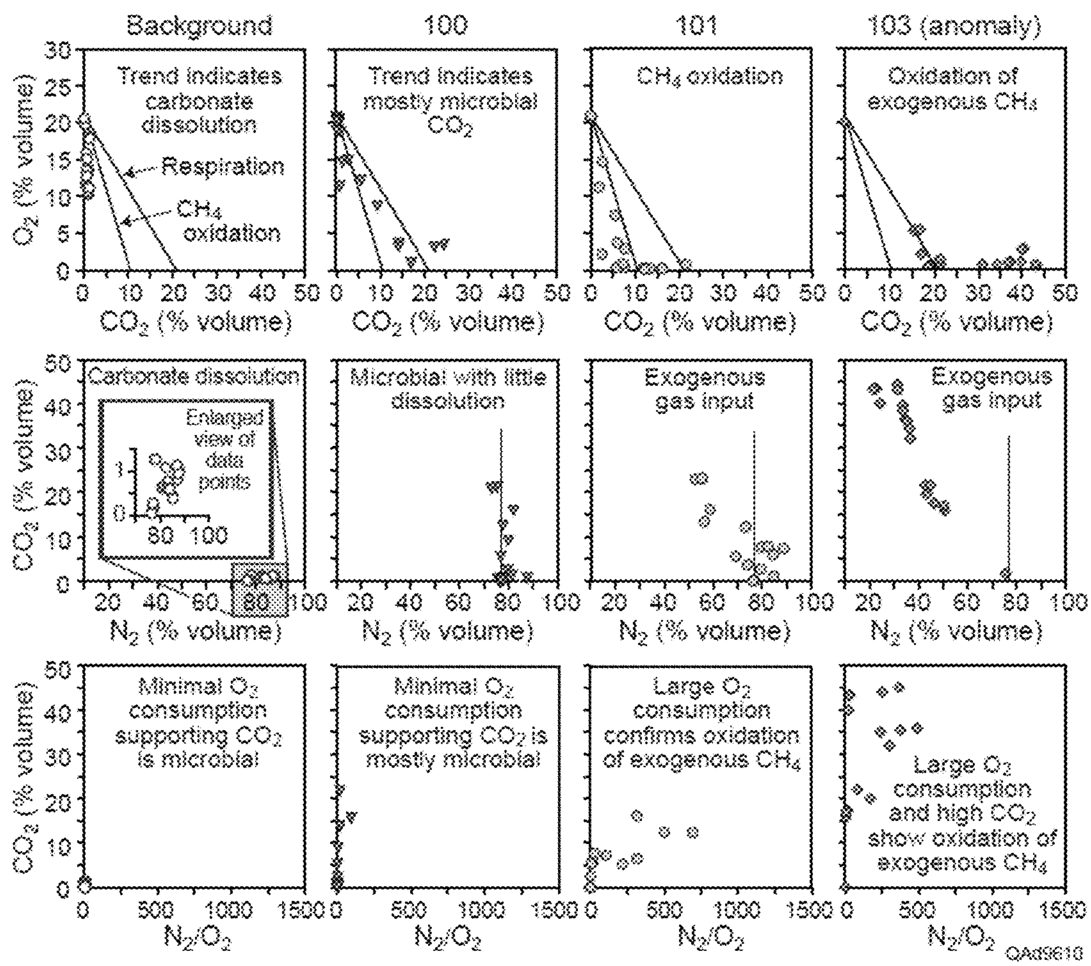

Floor
Respiration
Annulus
CH4 Oxidation
Slope
16
14
12
10
8
6
4
2
0
CO2 (vol %)
0
10
20
30
40
50
60
70
N2/O2

FIGURE 3



Background
100
101
103 (anomaly)
Trend indicates carbonate dissolution
Respiration
CH4 oxidation
Trend indicates mostly microbial CO2
CH4 oxidation
Oxidation of exogenous CH4
O2 (% volume)
CO2 (% volume)
Carbonate dissolution
Enlarged view of data points
Microbial with little dissolution
Exogenous gas input
Exogenous gas input
N2 (% volume)
Minimal O2 consumption supporting CO2 is microbial
Minimal O2 consumption supporting CO2 is mostly microbial
Large O2 consumption confirms oxidation of exogenous CH4
Large O2 consumption and high CO2 show oxidation of exogenous CH4
N2/O2
QAd9610

FIGURE 4

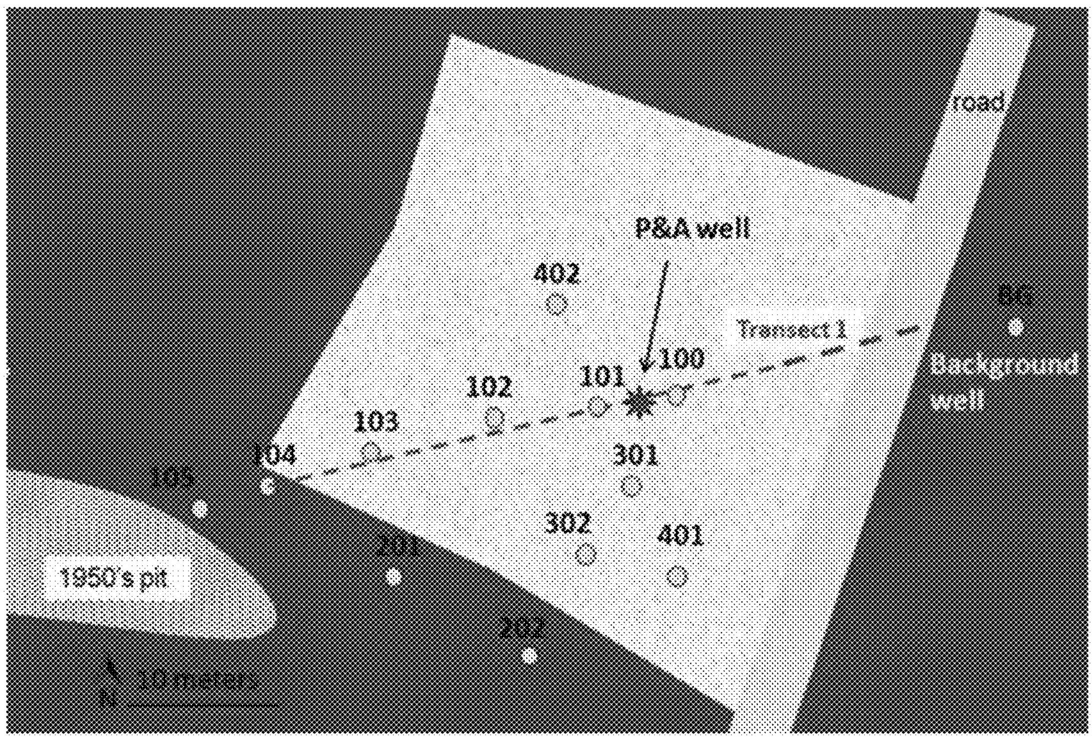

road
P&A well
402
BG
Transect 1
100
101
Background well
102
103
104
105
301
302
401
201
1950's pit
202
N
10 meters

FIGURE 5

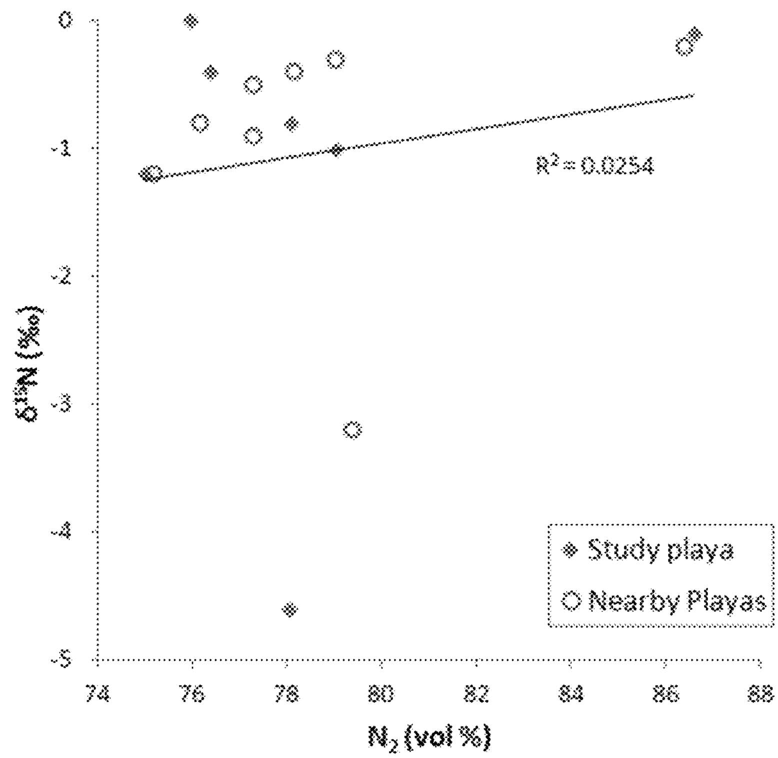


FIGURE 6

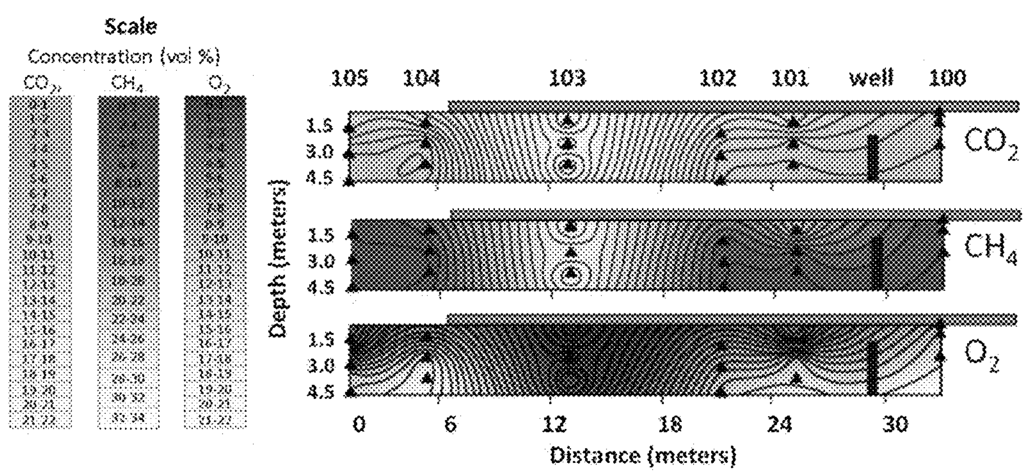


FIGURE 7

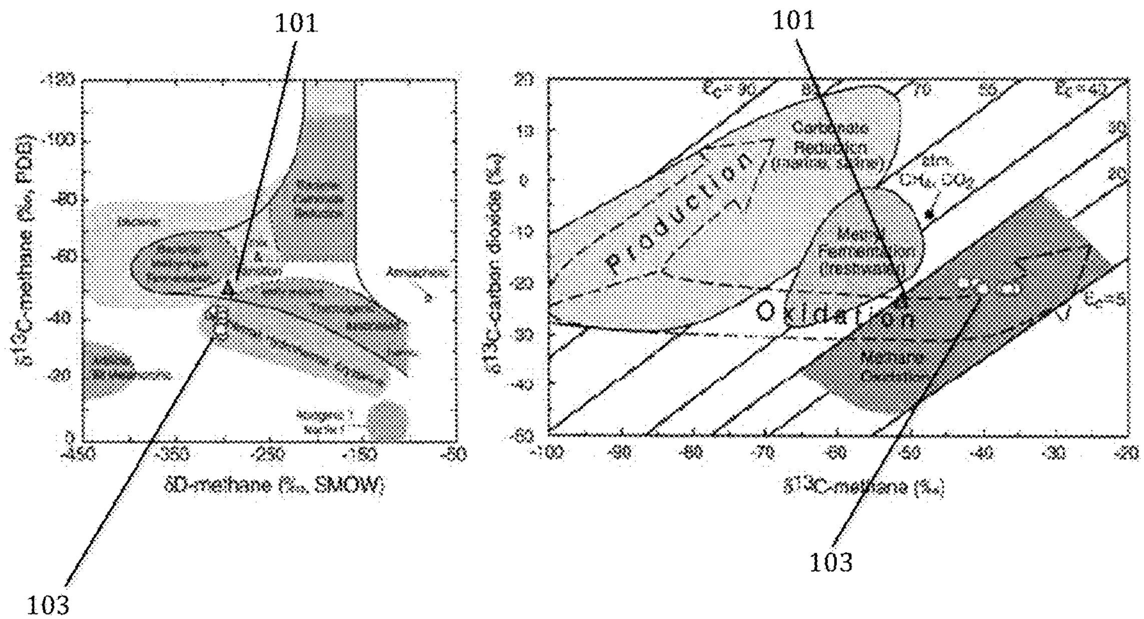

101
103
δD-methane (‰, SMOW)
δ13C-methane (‰, PDB)
Production
Oxidation
Carbonate Reduction
Methane Oxidation
δ13C-carbon dioxide (‰)
δ13C-methane (‰)
101
103

FIGURE 8

PROCESS-BASED APPROACH FOR THE DETECTION OF DEEP GAS INVADING THE SURFACE

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to U.S. Provisional Application Ser. No. 61/840,224, filed Jun. 27, 2013, the entire contents of which are incorporated herein by reference.

STATEMENT OF FEDERALLY FUNDED RESEARCH

This invention was made with U.S. Government support by the U.S. Department of Energy through the Office of the Governor of Texas (contract DE-FG04-9OAL65847) and the National Energy Technology Laboratory (contract DE FG26-05NT42590) through the Southeast Regional Carbon Sequestration Partnership. The government has certain rights in this invention.

TECHNICAL FIELD OF THE INVENTION

The present invention relates in general to the field of gas detection, and more particularly, to a novel process-based approach for the detection of deep gas invading the surface.

BACKGROUND OF THE INVENTION

Without limiting the scope of the invention, its background is described in connection with detecting gas in the vadose zone.

Measurement, monitoring and verification (MMV) will be required at geologic carbon storage (GCS) sites to document that storage effectively retains CO_2 in the subsurface [European Commission, 2009: US EPA, 2010a, b]. MMV can utilize many techniques deployed at a range of depths from the storage reservoir to the atmosphere, however techniques that monitor leakage through the near surface vadose zone are valuable because: (1) the vadose zone is the interface between subsurface storage and release to atmosphere, (2) gases moving through the shallow subsurface are easily and cheaply monitored, and (3) vadose zone monitoring can directly address concerns of landowners living above GCS sites [Shenk et al., 2011].

The most studied and currently widely accepted approach for vadose zone gas monitoring above GCS sites directly measures CO_2 concentrations either by extracting vadose zone gas through hollow push probes or by measuring CO_2 surface flux with accumulation chambers. Measurements are made in a grid pattern or in areas of concern, such as faults, fractures, or plugged and abandoned wells [Riding and Rochelle, 2009: Strazisar et al., 2009: Furche et al., 2010]. A minimum of 1 year of background concentration measurements is required prior to CO_2 injection to document natural seasonal ranges in vadose zone CO_2 apart from leakage. If CO_2 concentrations statistically exceed the background range during the lifetime of a GCS project, a storage formation release may be indicated. This approach is herein referred to as a "CO_2 concentration-based" approach.

A CO_2 concentration-based approach has several drawbacks: (1) high variability of CO_2 generated in situ could mask a moderate leakage signal; (2) 1 year of background characterization cannot account for CO_2 variability from climatic, land use, and ecosystem variations over the lifetime (tens to hundreds of years) of a storage project; (3) background measurements require a long lead time potentially hindering a project's progress; and (4) background CO_2 cannot be measured across all potential small diameter leak points within the area of review: therefore, if concerns arise in an area lacking local background measurements, no baseline data exist with which to compare monitored CO_2 concentrations.

SUMMARY OF THE INVENTION

In one embodiment, the present invention includes a method of determining the level of deep gas in a near surface formation without the need for background monitoring comprising: measuring CO_2, O_2, CH_4, and N_2 levels in percent by volume (or mole fraction) from one or more surface or near surface geological samples; adding the water vapor content to the measured CO_2, O_2, CH_4, and N_2 levels in percent by volume (or mole fraction); normalizing the gas mixture to 100% by volume or 1 atmospheric total pressure; and determining the ratios of: O_2 versus CO_2 to distinguish the general CO_2 production and consumption processes whether in-situ or from exogenous deep leakage CO_2; CO_2 versus N_2 to further distinguish whether CO_2 is being removed from the near surface formation or CO_2 is added from an exogenous deep leakage input; or CO_2 versus N_2/O_2 to determine the degree of oxygen influx, consumption, or both; wherein the ratios are indicative of natural in situ processes or from the exogenous deep leakage input. In one aspect, an in-situ vadose zone background level of carbon comprises at least one of biologic respiration, methane oxidation, or CO_2 dissolution. In another aspect, the presence of a deep gas source of carbon is indicated if the of N_2 is less than 76.4% in a water vapor saturated vadose zone environment. In another aspect if the vadose zone environment is dry, the presence of deep gas may be indicated if N_2 above 78%. In another aspect, if the level of O_2 is determined by gas chromatography without separation of O_2 and Argon peaks, the method further comprises subtracting the level of Argon from the level of O_2 to determine the actual level of O_2. In another aspect, the amount of Argon is calculated equal to $1/63 \times N_2$ concentration. In another aspect, the water vapor is saturated. In another aspect, the amount of water vapor is 2.1 to 2.4%, 2.2 to 2.35%, or 2.3%. In another aspect, the deep CO_2 gas versus CO_2 from biological respiration is in the near surface formation if the level of N_2 is below 76.4%. In another aspect, wherein an N_2/O_2 ratio greater than air indicates influx of air and/or O_2 consumption. In another aspect, the water vapor content is measured or estimated. In another aspect, the samples are collected in a sealed container and later analyzed in a laboratory.

In one embodiment, the present invention includes a method of determining the level of deep gas in a near surface formation without the need for background monitoring comprising: measuring CO_2, O_2, CH_4, and N_2 levels in percent by volume from one or more surface or near surface geological samples; adding the water vapor content to the measured CO_2, O_2, CH_4, and N_2 levels in percent by volume and normalizing the gas mixture to 100% by volume or 1 atmospheric total pressure; and determining the ratios of: O_2 versus CO_2 to distinguish in-situ vadose zone CO_2 from exogenous deep leakage CO_2; CO_2 versus N_2 to distinguish whether CO_2 is being removed from the near surface formation or CO_2 is added from an exogenous deep leakage input; and CO_2 versus N_2/O_2 to determine the degree of oxygen influx, consumption, or both; wherein the ratios are indicative of natural in situ CO_2 or CO_2 from the exogenous

deep leakage input. In another aspect, an in-situ vadose zone background level of carbon comprises at least one of biologic respiration, methane oxidation, or CO_2 dissolution. In another aspect, the presence of a deep gas source of carbon is indicated if the water saturated atmospheric value of N_2 is less than 76.4%. In another if the level of O_2 is determined by gas chromatography without separation of O_2 and Argon peaks, the method further comprises subtracting the level of Argon from the level of O_2 to determine the actual level of O_2. In another aspect, the amount of Argon is calculated equal to $1/63 \times N_2$ concentration. In another aspect, the water vapor is saturated. In another aspect, the amount of water vapor is 2.1 to 2.4%, 2.2 to 2.35%, or 2.3%. In another aspect, the deep CO_2 gas versus CO_2 from biological respiration is in the near surface formation if the level of N_2 is below 76.4%. In another aspect, wherein an N_2/O_2 ratio greater than air indicates influx of air and/or O_2 consumption. In another aspect, the water vapor content is measured or estimated. In another aspect, the samples are collected in a sealed container and later analyzed in a laboratory.

BRIEF DESCRIPTION OF THE DRAWINGS

For a more complete understanding of the features and advantages of the present invention, reference is now made to the detailed description of the invention along with the accompanying figures and in which:

FIG. **1** is a graph that shows soil gas data from a natural CO_2-rich playa site shown with general soil gas trends for common background processes of biologic respiration and methane oxidation (lines inside graph). Possible deviations are shown (inset). Gas compositions that plot below both the biological respiration and CH_4 oxidation lines indicate CO_2 dissolution and reaction with soil carbonate. Data representing a CO_2 leak from depth into the vadose zone would plot above these trend lines in the exogenous gas input field.

FIG. **2** shows three graphs that show a comparison of trends in CO_2 versus N_2 for various natural playa zones (slope, annulus, floor). Dashed line indicates atmospheric N_2 concentration in water vapor saturated soils (76.4%). Enrichment of N_2 concentrations above atmospheric values (samples to the right of the dashed line) indicates that the background process of CO_2 dissolution into recharging groundwater has occurred. If samples lie significantly to the left of the dashed line, exogenous gas input from deep reservoir leakage may be indicated.

FIG. **3** is a graph that shows the gas composition relationships of CO_2 versus N_2/O_2 for the playa study site. Trends for O_2 consumption during biologic respiration and CH_4 oxidation are shown. These relationships distinguish the amount of oxygen input and utilization. In a natural system with no exogenous input from depth, gases that undergo CO_2 dissolution and mixing with air will migrate to lower CO_2 concentrations and higher N_2/O_2 ratios.

FIG. **4** shows twelve graphs that summarize the vadose zone gas data from selected wells along a gas sampling transect extending from a background location to a vadose zone gas anomaly at the P-site at the Cranfield oil field. Systematic trends (previously discussed and identified in FIGS. **1**-**3**, at sites **100**, **101** and **103** of FIG. **5**) indicate that gas concentration relationships can distinguish natural background processes from exogenous gas input.

FIG. **5** is a map showing gas sampling locations at the p-site, Cranfield oilfield. Data are reported for stations BG, **100**, **101**, **103**. Additional drilling sites are labeled **102**, **104**, **105**, **201**, **202**, **301**, **302**, **401** and **402**. The main transect is indicated by the hashed line.

FIG. **6** is a graph of $\delta^{15}N$ versus N_2 concentrations for the study playa and for two other nearby playas in west Texas. Location information on additional playas as well as a discussion about nitrogen in playas can be found in Fryar et al. (2000). The data indicate little co-variation between the two parameters suggesting that although denitrification does occur, it is not significantly affecting nitrogen concentrations beneath playas.

FIG. **7** shows a cross section of CO_2 (≤21.4%), CH_4 (≤33.3%), and O_2 (0-21%) gas concentrations along the main gas sampling transect at the Cranfield oil field near the soil gas anomaly (centered at **103**, see FIG. **5** for numbered locations). Light colors indicate high concentrations; dark colors indicate low concentrations (scale at left). The cross section is presented to show the general distribution of gases in the subsurface. High concentrations of CO_2 and CH_4 correspond with low O_2. Gas diffusion gradients favor lateral migration near the anomaly and vertical migration away from the anomaly. O_2 appears to invade the subsurface at some distance from the anomaly epicenter migrating laterally at depth.

FIG. **8** shows an assessment of isotopic data from the Cranfield oil field using the system of Whiticar (1999). Blue triangle=station **101**; red circles=anomaly well **103**. The data indicate that CH_4 from well **103** originates from a deep exogenous source (i.e. the oil and gas reservoir) and CO_2 originates from methane oxidation. As expected, these relationships are less apparent at station **101**, farther from the anomaly. The exogenous source of gas and the process of methane oxidation are successfully identified using the process-based method of analysis.

DETAILED DESCRIPTION OF THE INVENTION

While the making and using of various embodiments of the present invention are discussed in detail below, it should be appreciated that the present invention provides many applicable inventive concepts that can be embodied in a wide variety of specific contexts. The specific embodiments discussed herein are merely illustrative of specific ways to make and use the invention and do not delimit the scope of the invention.

To facilitate the understanding of this invention, a number of terms are defined below. Terms defined herein have meanings as commonly understood by a person of ordinary skill in the areas relevant to the present invention. Terms such as "a", "an" and "the" are not intended to refer to only a singular entity, but include the general class of which a specific example may be used for illustration. The terminology herein is used to describe specific embodiments of the invention, but their usage does not delimit the invention, except as outlined in the claims.

A critical issue for geologic carbon sequestration is the ability to detect CO_2 leakage in the vadose zone. The present invention includes a new process-based approach to identify CO_2 that has leaked from deep geologic storage reservoirs into the shallow subsurface. Whereas current CO_2 concentration-based methods require years of background measurements to quantify variability of natural vadose zone CO_2, this new approach examines chemical relationships between vadose zone N_2, O_2, CO_2, and CH_4 to promptly distinguish a leakage signal from background CO_2. The method uses sequential inspection (1) O_2 versus CO_2 to distinguish in-situ vadose zone background processes (biologic respiration, methane oxidation, and CO_2 dissolution) from exogenous deep leakage input, (2) CO_2 versus N_2 to further distinguish dissolution of CO_2 from exogenous deep leakage input, and (3) CO_2 versus N_2/O_2 to assess the degree of atmospheric mixing/dilution occurring in the system. The approach was developed at a natural CO_2-rich analog site and successfully applied at a CO_2-enhanced oil recovery operation where deep gases migrated into the vadose zone. The ability to identify CO_2 leakage into the vadose zone without the need for background measurements could decrease uncertainty in leakage detection and expedite implementation of future geologic CO_2 storage projects.

To address the problem of separating signal (leaked) from background (in situ generated) CO_2 in the vadose zone, the present invention includes, for the first time, a powerful, yet simple geochemical approach to GCS leakage monitoring that does not require background monitoring. Instead, relationships among major fixed gases (CO_2, N_2, O_2, CH_4) are used to identify processes that produce and consume vadose zone CO_2. It was found herein that the major in situ vadose zone processes in this analysis can distinguish: biologic respiration, CH_4 oxidation, dissolution of CO_2 and reaction with soil carbonate, and atmospheric mixing.

Vadose zone processes. In the absence of carbon cycling processes, vadose zone gases are dominated by the atmosphere (in dry air, 78% N_2, 21% O_2, 0.039% CO_2, 1.8 ppm CH_4), which invades the subsurface via barometric pumping and diffusion. Root and microbial respiration in the vadose zone increases CO_2 and decreases O_2 relative to the atmosphere [Hanson et al., 2000] and is affected by temperature, soil moisture content, nutrient availability and oxygen supply which vary on diurnal, seasonal, and longer-term climatic timescales [e.g. Luo and Zhou, 2006]. Microbial respiration commonly produces CO_2 wherever organic matter, O_2, and soil moisture coexist, but when O_2 and other electron acceptors such as nitrate and sulfate are depleted, CH_4 is eventually produced [Konhauser, 2006]. If CH_4 migrates into oxic zones or if environmental change allows O_2 influx, CH_4 is oxidized to CO_2 [Whalen et al., 1990], potentially mimicking a storage formation leak signal. CH_4 oxidation is therefore important to identify wherever in situ CH_4 is produced or above oil and gas fields where CH_4 may seep from deep reservoirs into the vadose zone over geologic time. Soil gas CO_2 may be consumed by dissolution into infiltrating water and reaction with carbonate mineral phases [Striegl and Armstrong, 1990], forming a significant CO_2 sink. Vadose zone gas concentrations are also affected by invasion of atmosphere into the subsurface [Osterkamp and Wood, 1987], which can be induced by barometric pressure changes but may also result from pressure gradients caused by dissolution of gas into recharging water [Smith and Arah, 1991: Romanak, 1997: Nicot and Bennett, 1998].

Beginning with atmospheric gas concentrations, vadose zone processes alter soil gas geochemistry in predictable ways on the basis of either reaction stoichiometry or decoupling of gas components. Gas concentrations are measured in percent (volume or molar); therefore, any non-reactive addition or subtraction of a gas component will, by definition, dilute or concentrate, respectively, all other gases in similar proportions. The fixed composition of atmosphere, which dominates the vadose zone in the absence of background or leakage processes, provides the starting point from which to assess reactions. N_2 is a good measure of dilution and/or enrichment of a gas mixture owing to its abundance in air and non-reactivity which is compromised only in extreme cases of denitrification [Fryar et al., 2000]. Denitrification can be identified by N_2 that is depleted in ^{15}N relative to atmosphere ($\delta^{15}N$=0‰) [Mariotti et al., 1981], or by Ar/N_2 that is significantly less than 0.0119 [Martin et al, 1995].

The process in soils posing the greatest challenge to CO_2 concentration based monitoring is CO_2 production by oxidation of organic matter during aerobic microbial respiration. This process is represented as:

$$CH_2O+O_2 \rightarrow CO_2+H_2O \tag{1}$$

where O_2 consumption and CO_2 production result in a predictable trend (slope of −1) originating from atmospheric concentrations) on a graph of CO_2 versus O_2 (FIG. **1**). During methane oxidation,

$$CH_4+2O_2 \rightarrow CO_2+2H_2O \tag{2}$$

O_2 consumption and CO_2 production produce a trend with a slope of −2 on the same graph. CO_2 values higher than expected from corresponding O_2 values signal an exogenous CO_2 source, indicating a potential leak, and CO_2 values lower than expected from corresponding O_2 values signal a CO_2 sink.

Study sites. The process-based leakage detection approach was developed at a natural CO_2-rich ephemeral playa lake in west Texas, USA. Here, known vadose zone processes were coupled with their corresponding soil gas signatures. This information was then successfully applied at an oil field in Mississippi at the site of a plugged and abandoned well to identify anomalous near-surface CO_2 and CH_4 soil gas signals.

Playa Natural Analog: The playa lakes of west Texas are broad, gently sloping circular basins (~1 to 2 km in diameter) that accumulate and transmit surface runoff through a thick (~60 m) vadose zone. Geomorphic areas associated with playas, which include: slope, annulus, and floor, systematically differ in water flux, organic carbon content, and inorganic soil carbonate, creating spatial variability in the main factors that affect natural vadose zone CO2 production and consumption [Osterkamp and Wood, 1987; Romanak, 1997]. These systematic differences provide an opportunity to link various natural CO2 cycling processes to their vadose zone soil gas signatures. The low-angle playa slope defines the outer edge of the playa basin and transmits storm runoff onto playa floors [Gustayson and Winkler, 1988]. The annulus, a sort of "bathtub ring" defined by a break in slope around the lake's shoreline, transmits water through silty sediments only during high water levels [Hovorka, 1996; Scanlon et al., 1997]. Organic-rich clays and silty clay loams of the flat playa floor pond water before transmitting it along shrink-swell fractures and root tubules through clay deposits [Hovorka, 1996: Scanlon et al., 1997]. Beneath playa floors, dissolved organic carbon is microbially oxidized to produce CO2 which dissolves soil carbonate to create piping and secondary pores as large as 7 mm in diameter (Osterkamp and Wood, 1987).

The specific playa studied herein is located at 35° 25' 2.2" N, 101° 30' 8.4" W, with a diameter of 0.8 km. Soil gas collected during 10 sampling trips between August 1992 and May 1995 was analyzed for CO2, O2, N2, CH4, δ13C of CO2, and 15N of N2 from 23 stations containing 54 semi-permanent soil gas wells at depths ranging from 0.6 to 13.7 m. Stations were installed along radial transects extending through slope, annulus and floor areas to identify variations in soil gas concentrations under varying environmental conditions.

Industrial Oil Field Site. Methods applied at the playa study were applied at an area named the P-site at the Cranfield oil field 18 km east of Natchez Miss., USA (31° 34'

11.8" N, 91° 9' 27.4" W) where oil production from the Tuscaloosa Formation (3050 m began in 1944 [Hines, 1950]. Depletion of the field by 1966 was followed by plugging and abandonment of approximately 100 wells in the 31 km^2 oil field. CO_2-enhanced oil recovery (EOR) began in 2008 by Denbury Resources Inc.

Vadose zone monitoring at the P-site began before local CO_2 injection. At the site, 13 multi-depth gas sampling stations with a total of 39 gas wells as deep as 3 m were installed in various locations around an 1124 m^2 gravel pad. One transect extends from an open pit used during 1950s oil production, across the gravel pad near a plugged and abandoned well, and out onto a grassy clearing defined as a background location. Data from portions of this major transect collected over a one-year period.

At both study sites, semi-permanent gas wells were used to sample gas from different depths within the vadose zone (see Well Station Construction, below). This installation type provides: (1) depth profiles of subsurface gas distribution, (2) potential for repeat sampling with exact spatial matching, and (3) sediment samples for assessment of parameters important to reactive transport modeling, soil contamination, or soil/water interactions. Boreholes were as deep as 14 m and well placement was targeted to areas of concern identified through reconnaissance sampling using a standard push probe.

Well Station Construction. Semi-permanent soil gas sampling stations were comprised of multiple sampling tubes (0.64-cm copper tubing at the playa and 0.32-cm stainless steel tubing at Cranfield) installed at depths of interest within each 5-cm diameter borehole. [Note: Wells can generally be installed in any size borehole that will accommodate the number of wells desired however larger diameter holes require more material for back-filling. Generally 5 cm diameter boreholes are desirable and will accommodate up to four wells]. Before drilling, all underground infrastructures were identified to avoid hitting gas or electrical lines. At the down-hole end of the Cranfield gas sampling wells, 152 mm stainless steel mesh screens (Geoprobe 15-cm vapor implants) were connected with Swagelok gas-tight fittings. Screens were set in 20-30 cm of quartz sand. The borehole was then backfilled with wetted bentonite clay chips to isolate the sampling interval until the next sampling level was reached. The process was repeated until all gas sampling wells were set in sand pack and their sampling intervals isolated with bentonite. Each gas sampling well was carefully labeled with its depth and topped with either a rubber tip (playa) or a noflow Swagelok quick connect stem (SS-QM2-D-200) that stops air from entering the tube until it is joined to the sampling hose with a quick connect body (SS-QM2-B-200) (Cranfield). All gas well tubing was cut at similar heights above ground surface (~0.3 to 0.5 meters). When the borehole was filled to within 0.5 m of ground surface, a PVC protector pipe was installed over the sampling tubes, inserted into the remaining space within the borehole and secured by adding wetted bentonite around the annulus to hold it in place. The pipe was capped and labeled and protected the gas sampling wells from environmental damage.

Field GC Analysis. A Masterflex E/S portable peristaltic pump was used to draw soil-gas from wells at a flow rate of approximately 50 to 100 cc/min and deliver the sample to the gas chromatograph (GC) through tygon tubing directly plumbed to the inlet of the GC sample loop. During sampling, either an in-line pressure gauge for monitoring well pressure or a flow meter for monitoring flow rate were used to verify that no vacuum pressure developed risking dilution with ambient air or cross contamination from other sampling depths. Prior to GC analysis, the sample line to the well was purged for a sufficient time to void 2-3 well/sample line volumes. Sampling at each well continued until three runs with stable concentrations within ±10% relative difference) for each analyte were obtained. The GC was calibrated using air and certified low and high standard gas mixtures (Scot brand) spanning expected nominal concentration ranges before, during, and after each day's sampling. The precision for both detectors is ±2%.

On-site analysis of major gas compounds (CO_2, O_2, N_2, and CH_4) was accomplished at both sites using a portable gas chromatograph (SRI 8610) fixed with a CTR2 binary column (Porapak Q and molecular sieve), thermal conductivity (TCD) and flame ionization (FID) detectors, hydrogen carrier gas at various flow rates (35-46 mls/min), and isothermal temperatures of 30-45° C. A methanizer on the FID brought detection limits for CO_2 down to atmospheric concentrations. This chromatographic method does not separate argon (Ar) from O_2, therefore, Ar was estimated at 1/83 of N2 and subtracted from the O_2 measurement which is acceptable when denitrification is insignificant N2 [Smith and Arah, 1991]. 2.2% water vapor representing saturated water vapor pressure was added to all measurements. All sample measurements were normalized to 100% for comparison purposes due to slight differences in the inlet pressures at the GC sample loop from variations in pumping rates.

Laboratory Analysis. Gas samples for δ13C and δ15N were collected in stainless steel gas cylinders with Swagelok fittings at the playa site and in pre-evacuated Cali 5-bond gas bags at Cranfield. Carbon isotopes for the playa study were analyzed by mass spectrometer at Coastal Isotope Laboratories in Austin Tex. (δ13C relative to PDB standard with a precision of ±0.2%). δ15N was measured by mass spectrometer at the Department of Environmental Sciences at the University of Virginia with atmospheric nitrogen as the standard and precision±0.15%). δ13C of CO2 and CH4 and δD of CH4 at Cranfield were collected in preevacuated Cali 5-bond gas bags and analyzed at Isotech Laboratories (Champaign, Ill.) using a GC-CIRMS system. This method employs a GC combustion unit interfaced with a mass spectrometer (Delta V Plus or Delta Plus Advantage). Samples are injected into the GC split/splitless injector and are separated by the GC column. Each individual hydrocarbon (CH4) component is combusted and the resultant CO2 is introduced directly into the mass spectrometer. Hydrogen isotopic values for methane are completed using the same system, but the gas is channeled through a high-temperature pyrolysis furnace instead of through the combustion furnace. The pyrolysis furnace converts methane into H2 and carbon, and the H2 gas is introduced directly into the mass spectrometer. Nitrogen isotopic data for elemental nitrogen (N2) is generated using the same system. For measurement of isotopes of CO2, the gas does not pass through a combustion furnace but is channeled directly from the GC outlet to the collection trap. Stated precision for δ13C is ±0.3% and for δD±2.0%.

Major gas compounds (CO_2, O_2, N_2, and CH_4) were analyzed on-site at both study areas using a portable gas chromatograph. Samples were also collected for laboratory isotope analyses including $\delta^{13}C$ of CO_2 and CH_4, δD of CH_4, and ^{15}N of N_2. Playa samples were collected in stainless steel gas cylinders with Swagelok fittings and analyzed either by mass spectrometer at Coastal Laboratories, Austin, Tex. ($\delta^{13}C$ of CO_2) or at the University of Virginia ($\delta^{15}N$ of N_2). Isotopes of Cranfield gases ($\delta^{13}C$ of

CO_2 and CH_4, and δD of CH_4) were collected in Cali-5-bond bags and analyzed at Isotech Laboratories, Champaign, Ill. by mass spectrometer.

Natural Analog Playa Site. In the playa, maximum concentrations of CO_2 (slope: 5.0%, annulus: 10.5%, floor: 17.2%) and CH_4 (slope: 0%, annulus: 2.2%, floor: 0.9%), coupled with minimum O_2 (slope: 15.6%, annulus: 0.1%, and floor 0.0%) indicate that microbial CO_2 and CH_4 production is relatively low in the slope, where organic carbon content and water flux is low, and high in the floor, where organic carbon content and water flux is high. The annulus is a transitional zone, behaving like the slope when dry and the floor when high water levels allow water infiltration through annulus sediments.

FIG. **5** is a map showing gas sampling locations at the p-site, Cranfield oilfield. Data are reported for stations BG, **100**, **101**, **103**. Additional drilling sites are labeled **102**, **104**, **105**, **201**, **202**, **301**, **302**, **401** and **402**. The main transect is indicated by the hashed line.

Gas compositions from the slope and annulus, and a few from the floor, cluster between trends for microbial respiration and CH_4 oxidation on a graph of CO_2 versus O_2 with some analytical scatter (FIG. **1**). Many samples from the playa floor lie below both trend lines indicating a loss of CO_2 from the gas phase. Samples that indicate this loss of CO_2 (most gas compositions from the floor and some from the annulus) generally also exhibit N_2 values enriched above atmospheric values (FIG. **2**). Nitrogen isotope ratios of gas sampled from three area playas show insignificant denitrification, indicated by a lack of covariation between N_2 and ^{15}N(R^2=0.0254) for 15 samples (FIG. **6**). Comparison of N_2 and CO_2 concentrations from each playa zone (FIG. **2**) shows the following relationships: (1) N_2 values in the slope (74.0-79.0%) resemble those of the atmosphere, (2) N_2 values in the floor (74.8-92.4%) are predominantly enriched relative to the atmosphere, and (3) N_2 signatures in the annulus (74.3-98.1%) are mixed, depending on whether the annulus was wet and undergoing infiltration or dry.

N_2 concentrations enriched relative to the atmosphere suggest the dissolution of CO_2 into recharging groundwater enhanced by concurrent dissolution of soil carbonate. The loss of CO_2 from the gas phase enriches the percent concentration of N_2 above atmospheric values. N_2 enrichment is augmented by advection of the atmosphere into soil pores driven by the pressure differential created from loss of CO_2 gas [Smith and Arah, 1991: Nicot and Bennett, 1998].

Oxygen consumption during CH_4 oxidation, and to a lesser degree from microbial respiration, is identified by N_2/O_2 above the atmospheric ratio of 3.8 (FIG. **3**), in the absence of significant denitrification. Whereas both atmospheric mixing and CO_2 dissolution retain a 3.8 ratio, O_2 consumption increases this ratio. At the playa, O_2 consumption from microbial respiration increases N_2/O_2 to as high as 10, whereas CH_4 oxidation coupled with air influx increases this ratio to as high as 60 (FIG. **3**). N_2/O_2 is therefore an indicator of the magnitude of oxygen influx and consumption, which can be an indicator of CH_4 oxidation and discriminates microbial respiration and carbonate dissolution from CH_4 oxidation which is an especially important distinction in hydrocarbon fields where oxidized CH_4 seepage could be mistaken for a CO_2 leak.

Industrial Site Cranfield Results. The base concept that background processes can be distinguished from a leakage signal using soil gas geochemical relationships was tested at the Cranfield oil field. Here, a persistent CO_2 (44.7%) and CH_4 (33.5%) anomaly is centered along a 55 m soil gas sampling transect near a plugged and abandoned well (FIGS. **5** and **7**). CO_2 and CH_4 concentrations decrease and O_2 generally increases away from the anomaly along the 43 m that separate the anomaly and background locations. Gas sampled from the anomaly shows isotopic relationships for CH_4 ($\delta^{13}C$ −36.7 to −42.4‰: δD −305.0 to −310.2‰) and CO_2 ($\delta^{13}C$, −18.6 to −19.8‰) that are consistent with a deep thermogenic CH_4 source and CO_2 derived from CH_4 oxidation (Whiticar, 1999: FIG. **8**. These data confirm that the vadose-zone anomaly is exogenous gas originating from depth and provides an unambiguous setting in which to test the potential of the process-based method to perform in less obvious leakage detection scenarios.

To further confirm the methodology, key gas concentration relationships (CO_2 vs. O_2, CO_2 vs. N_2, and CO_2 vs. N_2/O_2) developed at the playa site were systematically observed from the background well toward the anomaly (FIG. **4**). In the background well, gas compositions fall well below the respiration and CH_4 oxidation trends on a graph of O_2 versus CO_2 indicating the background process of CO_2 dissolution and reaction with soil carbonate. In situ processes are further supported by N_2 concentrations enriched with respect to the atmosphere. O_2/N_2 is near atmospheric ratios indicating no CH_4 oxidation.

As the anomaly is approached along the transect, soil gas relationships between CO_2 and O_2 shift systematically toward the CH_4 oxidation trend line, then to low O_2 concentrations along that line, and finally to the right of the biologic respiration trend in the leakage field (FIG. **4**). This progressive transformation represents an increasing magnitude of CH_4 oxidation as the anomaly is approached which eventually manifests as an exogenous source plotting in the leakage field. N_2 versus CO_2 also shifts as the anomaly is approached from a background CO_2 dissolution signal to one that signifies input of exogenous gas (N_2 concentrations<atmospheric values). N_2/O_2 ratios much greater than air correctly indicate persistent CH_4 oxidation and influx of air.

The present invention provides for the first time a new approach to separate leakage signal in the vadose zone above GCS sites from relatively complex natural CO_2 cycling processes without the need for background data. The approach uses three major soil gas concentration relationships (CO_2 vs. O_2, CO_2 vs. N_2, and CO_2 vs. N_2/O_2) to identify the vadose zone processes of biologic respiration, CH_4 oxidation, soil carbonate and CO_2 dissolution, atmospheric mixing, and input of exogenous gas (CO_2 and/or CH_4). Natural background processes were identified at a CO_2-rich playa lake in west Texas and using these techniques that were then successfully applied at an industrial oil field site near Cranfield, Miss., where exogenous gas input from depth reached the surface. At the Cranfield site, gas concentration relationships indicating natural processes shifted systematically to those indicating an exogenous gas source as a surface gas anomaly was approached. Success of the process-based approach to identify deep gas in the vadose zone at an industrial site represents a significant advance in our ability to detect CO_2 leakage from depth into the vadose zone at CO_2 storage sites.

It is contemplated that any embodiment discussed in this specification can be implemented with respect to any method, kit, reagent, or composition of the invention, and vice versa. Furthermore, compositions of the invention can be used to achieve methods of the invention.

It will be understood that particular embodiments described herein are shown by way of illustration and not as limitations of the invention. The principal features of this invention can be employed in various embodiments without departing from the scope of the invention. Those skilled in the art will recognize, or be able to ascertain using no more than routine experimentation, numerous equivalents to the specific procedures described herein. Such equivalents are considered to be within the scope of this invention and are covered by the claims.

All publications and patent applications mentioned in the specification are indicative of the level of skill of those skilled in the art to which this invention pertains. All publications and patent applications are herein incorporated by reference to the same extent as if each individual publication or patent application was specifically and individually indicated to be incorporated by reference.

The use of the word "a" or "an" when used in conjunction with the term "comprising" in the claims and/or the specification may mean "one," but it is also consistent with the meaning of "one or more," "at least one," and "one or more than one." The use of the term "or" in the claims is used to mean "and/or" unless explicitly indicated to refer to alternatives only or the alternatives are mutually exclusive, although the disclosure supports a definition that refers to only alternatives and "and/or." Throughout this application, the term "about" is used to indicate that a value includes the inherent variation of error for the device, the method being employed to determine the value, or the variation that exists among the study subjects.

As used in this specification and claim(s), the words "comprising" (and any form of comprising, such as "comprise" and "comprises"), "having" (and any form of having, such as "have" and "has"), "including" (and any form of including, such as "includes" and "include") or "containing" (and any form of containing, such as "contains" and "contain") are inclusive or open-ended and do not exclude additional, unrecited elements or method steps.

The term "or combinations thereof" as used herein refers to all permutations and combinations of the listed items preceding the term. For example, "A, B, C, or combinations thereof" is intended to include at least one of: A, B, C, AB, AC, BC, or ABC, and if order is important in a particular context, also BA, CA, CB, CBA, BCA, ACB, BAC, or CAB. Continuing with this example, expressly included are combinations that contain repeats of one or more item or term, such as BB, AAA, AB, BBC, AAABCCCC, CBBAAA, CABABB, and so forth. The skilled artisan will understand that typically there is no limit on the number of items or terms in any combination, unless otherwise apparent from the context. In certain embodiments, the present invention may also include methods and compositions in which the transition phrase "consisting essentially of" or "consisting of" may also be used.

As used herein, words of approximation such as, without limitation, "about", "substantial" or "substantially" refers to a condition that when so modified is understood to not necessarily be absolute or perfect but would be considered close enough to those of ordinary skill in the art to warrant designating the condition as being present. The extent to which the description may vary will depend on how great a change can be instituted and still have one of ordinary skilled in the art recognize the modified feature as still having the required characteristics and capabilities of the unmodified feature. In general, but subject to the preceding discussion, a numerical value herein that is modified by a word of approximation such as "about" may vary from the stated value by at least ±1, 2, 3, 4, 5, 6, 7, 10, 12 or 15%.

All of the compositions and/or methods disclosed and claimed herein can be made and executed without undue experimentation in light of the present disclosure. While the compositions and methods of this invention have been described in terms of preferred embodiments, it will be apparent to those of skill in the art that variations may be applied to the compositions and/or methods and in the steps or in the sequence of steps of the method described herein without departing from the concept, spirit and scope of the invention. All such similar substitutes and modifications apparent to those skilled in the art are deemed to be within the spirit, scope and concept of the invention as defined by the appended claims.

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What is claimed is:

1. A method of determining a level of deep gas in a near surface formation without a need for background monitoring comprising:

- measuring CO_2, O_2, CH_4, and N_2 levels in percent by volume from one or more surface or near surface geological samples;
- transforming the measured CO_2, O_2, CH_4, and N_2 levels by adding water vapor content to the measured CO_2, O_2, CH_4, and N_2 levels in percent by volume;
- normalizing the CO_2, O_2, CH_4, and N_2 levels to 100% by volume or 1 atmosphere total pressure to generate normalized CO_2, O_2, CH_4, and N_2 levels;
- determining the ratios of:
  - the normalized O_2 level versus the normalized CO_2 level to distinguish in-situ vadose zone CO_2 from exogenous deep leakage CO_2; and
  - the normalized CO_2 level versus the normalized N_2 level to distinguish whether CO_2 is being removed from the near surface formation or CO_2 is added from an exogenous deep leakage input; or the normalized CO_2 level versus the normalized N_2 level divided by the normalized O_2 level to determine a degree of oxygen influx, consumption, or both oxygen influx and consumption; and
- evaluating the ratios to determine whether CO_2 present in the surface or near surface geological samples is from natural in-situ CO_2 or CO_2 from exogenous deep leakage without a need for background monitoring, wherein evaluating includes identifying CO_2 from exogenous deep leakage if the normalized N_2 level is less than 78% under dry conditions, wherein evaluating includes identifying CO_2 from natural in-situ CO_2 if the normalized N_2 level is about 78% under dry conditions, or wherein evaluating includes identifying air influx into the near surface formation if the normalized N_2 level divided by the normalized O_2 level is greater than a ratio of O_2 to N_2 in air.

2. The method of claim **1**, wherein an in-situ vadose zone background level of carbon comprises at least one of biologic respiration, methane oxidation, or CO_2 dissolution.

3. The method of claim **1**, wherein a presence of a deep gas source of carbon is indicated if the normalized N_2 level under water saturated conditions is less than 76.4%.

4. The method of claim **1**, wherein if the normalized O_2 level is determined by gas chromatography without separation of O_2 and Argon peaks, the method further comprises subtracting an amount of Argon from the normalized O_2 level to determine an actual O_2 level.

5. The method of claim **4**, wherein the amount of Argon is calculated equal to 1/63× the normalized N_2 level.

6. The method of claim **1**, wherein the water vapor content corresponds to water saturated conditions.

7. The method of claim **1**, wherein an amount of the water vapor content is 2.1 to 2.4%.

8. The method of claim **1**, further comprising installing gas probes into the near surface formation for measuring the CO_2, O_2, CH_4, and N_2 levels.

9. The method of claim **1**, wherein the water vapor content is measured or estimated.

10. The method of claim **1**, wherein the one or more surface or near surface geological samples are collected in a sealed container and later analyzed in a laboratory.

11. A method of determining a level of deep gas in a near surface formation without a need for background monitoring comprising:

- measuring CO_2, O_2, CH_4, and N_2 levels in percent by volume from one or more surface or near surface geological samples;
- transforming the measured CO_2, O_2, CH_4, and N_2 levels by adding water vapor content to the measured CO_2, O_2, CH_4, and N_2 levels in percent by volume;
- normalizing the CO_2, O_2, CH_4 and N_2 levels to 100% by volume or 1 atmosphere total pressure to generate normalized CO_2, O_2, CH_4 and N_2 levels;
- determining the ratios of:
  - the normalized O_2 level versus the normalized CO_2 level to distinguish in-situ vadose zone CO_2 from exogenous deep leakage CO_2;
  - the normalized CO_2 level versus the normalized N_2 level to distinguish whether CO_2 is being removed from the near surface formation or CO_2 is added from an exogenous deep leakage input; and
  - the normalized CO_2 level versus the normalized N_2 level divided by the normalized O_2 level to determine a degree of oxygen influx, consumption, or both oxygen influx and consumption; and
- evaluating the ratios to determine whether CO_2 present in the surface or near surface geological samples is from natural in-situ CO_2 or CO_2 from exogenous deep leakage without a need for background monitoring, wherein evaluating includes identifying CO_2 from exogenous deep leakage if the normalized N_2 level is less than 78% under dry conditions, wherein evaluating includes iden-

tifying CO_2 from natural in-situ CO_2 if the normalized N_2 level is about 78% under dry conditions and wherein evaluating includes identifying air influx into the near surface formation if the normalized N_2 level divided by the normalized O_2 level is greater than a ratio of O_2 to N_2 in air.

12. The method of claim **11**, wherein an in-situ vadose zone background level of carbon comprises at least one of biologic respiration, methane oxidation, or CO_2 dissolution.

13. The method of claim **11**, wherein the presence of a deep gas source of carbon is indicated if the normalized N_2 level under water saturated conditions is less than 76.4%.

14. The method of claim **11**, wherein if the normalized O_2 level is determined by gas chromatography without separation of O_2 and Argon peaks, the method further comprises subtracting an amount of Argon from the normalized O_2 level to determine an actual O_2 level.

15. The method of claim **14**, wherein the amount of Argon is calculated equal to 1/63× the normalized N_2 level.

16. The method of claim **11**, wherein the water vapor content corresponds to water saturated conditions.

17. The method of claim **11**, wherein an amount of the water vapor content is 2.1 to 2.4%.

18. The method of claim **11**, further comprising installing probes into the near surface formation for measuring the CO_2, O_2, CH_4, and N_2 levels.

19. The method of claim **11**, wherein the water vapor content is measured or estimated.

20. The method of claim **11**, wherein the one or more surface or near surface geological samples are collected in a sealed container and later analyzed in a laboratory.

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